

PCT

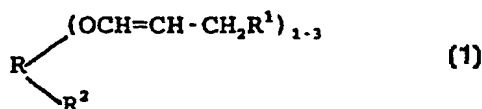
WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>6</sup> : C07C 43/16, 43/215, 69/12, 69/54, 69/96, 271/12, 271/28</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 99/10303</b> (43) International Publication Date: 4 March 1999 (04.03.99)</p>
<p>(21) International Application Number: PCT/US98/17110 (22) International Filing Date: 19 August 1998 (19.08.98) (30) Priority Data: 08/918,829 26 August 1997 (26.08.97) US (71) Applicant: RESEARCH CORPORATION TECHNOLOGIES, INC. [US/US]; Suite 600, 101 N. Wilmot Road, Tucson, AZ 85711-3335 (US). (72) Inventor: CRIVELLO, James; 756 Carlton Road, Clifton Park, NY 12065 (US). (74) Agents: DiGIGLIO, Frank, S. et al.; Scully, Scott, Murphy &amp; Presser, 400 Garden City Plaza, Garden City, NY 11530 (US).</p>		<p>(81) Designated States: CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>With amended claims.</i></p>

(54) Title: RADIATION-CURABLE PROPENYL COMPOUNDS, USES THEREOF, AND COMPOSITIONS CONTAINING THEM



(57) Abstract

Disclosed are compounds of formula (1): R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms; R<sup>1</sup> is -H or -CH<sub>3</sub>; R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloxy, methacryloxy, or A-(Het)<sub>0-1</sub>C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-; or R<sup>2</sup> is -L-X-(L-R-(OCH=CH-CH<sub>2</sub>R<sup>1</sup>)<sub>n</sub>)<sub>1-3</sub> wherein X has any of the structures -Ph<sub>0-1</sub>-C<sub>6</sub>H<sub>4</sub>-Ph<sub>0-1</sub>-Ph<sub>0-1</sub>-(cyclo-C<sub>5-20</sub>-alkyl)-Ph<sub>0-1</sub>-, -Ph-Ph-, or -Ph-, wherein Ph is phenylene and a is 1 to 20; -C<sub>f</sub>H<sub>2f</sub>C(O)C<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>C(O)OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>PhC<sub>g</sub>H<sub>2g</sub>-, or -C<sub>f</sub>H<sub>2f</sub>C(O)NHC<sub>g</sub>H<sub>2g</sub>-, wherein f and g are each 1 to 12; and each L is independently a chemical bond or -C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-, provided that each R is bonded to an oxygen atom of L; or X is -C(O)-, each L is a chemical bond, and i is 1. Also disclosed are methods and compositions useful in the radiation-induced polymerization of such compounds.

BEST AVAILABLE COPY

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

RADIATION-CURABLE PROPENYL COMPOUNDS,  
USES THEREOF, AND COMPOSITIONS CONTAINING THEM

1           The present invention relates to novel  
radiation-curable propenyl compounds, to radiation-  
curable compositions containing such compounds, and to  
processes for forming radiation-cured products from  
5   such compounds and compositions.

          Radiation curing has become an important and  
useful technique for applying and curing coatings,  
inks, and adhesives. As described herein, radiation  
curing involves presenting a radiation-curable  
10   polymer, typically in combination with a photo-  
initiator, and exposing the composition to radiation  
in the form of ultraviolet or electron-beam radiation  
to cause the radiation-curable compound to polymerize.

          Radiation curing presents many advantages,  
15   such as high rates of throughput, low energy  
requirements, and low equipment costs. In addition,  
it is advantageous that users are able to avoid using  
a solvent when the composition to be radiation-cured  
is prepared. Solvents typically would lead to  
20   environmental and/or safety hazards, and would require  
additional equipment and handling steps to remove the  
solvent.

          Propenyl compounds useful in the preparation  
of polymeric coatings and the like via  
25   photopolymerization are disclosed in, for instance,  
U.S. Patent No. 5,486,545 and U.S. Patent No.  
5,567,858. However, there remains a need for  
radiation-curable compounds, photopolymerizable or  
otherwise, which provide improved versatility and

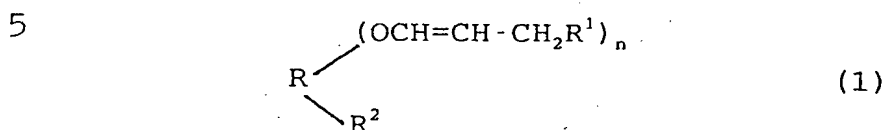
30

35

- 2 -

which can be formulated into a variety of coatings,  
1 films and the like readily and rapidly.

The present invention comprises compounds of  
the formula (1)



wherein n is an integer from 1 to 3;

10 R is linear, branched or cyclic alkyl  
containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon  
atoms which is optionally substituted with phenyl and  
15 two consecutive carbon atoms of which are optionally  
bonded to an oxygen atom to form an epoxy ring,  
phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>0.1</sub>-  
C(O)O- wherein A is alkyl containing 1 to 20 carbon  
atoms, and (Het) is -O- or -NH-;

20 or R<sup>2</sup> is -L-X-(L-R-(OCH=CH-CH<sub>2</sub>R<sup>1</sup>)<sub>n</sub>)<sub>1</sub>

wherein X has any of the structures -Ph<sub>0.1</sub>-C<sub>a</sub>H<sub>2a</sub>-Ph<sub>0.1</sub>-  
-Ph<sub>0.1</sub>-(cyclo-C<sub>5-20</sub>-alkyl)-Ph<sub>0.1</sub>-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

-C<sub>f</sub>H<sub>2f</sub>C(O)C<sub>g</sub>H<sub>2g</sub> -C<sub>f</sub>H<sub>2f</sub>OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>C(O)OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>PhC<sub>g</sub>H<sub>2g</sub>-,  
25 or -C<sub>f</sub>H<sub>2f</sub>C(O)NHC<sub>g</sub>H<sub>2g</sub>-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

provided that each R is bonded to an oxygen atom of L,

30

35

- 3 -

and i is an integer from 1 to 3; or X is -C(O)-, each  
1 L is a chemical bond, and i is 1.

Furthermore, the compounds in formula (1),  
can contain up to (n-1) (OCH<sub>2</sub>CH=CHR<sup>1</sup>) groups in place of  
(OCH=CH-CH<sub>2</sub>R<sup>1</sup>) groups.

5 The present invention is further directed to  
compositions comprising one or more compounds of said  
formula (1), and also comprising one or more  
photoinitiators in an amount effective to mediate  
polymerization of said compound when the composition  
10 is irradiated with, for instance, ultraviolet  
radiation or electron beam radiation.

Still further, the present invention is  
directed to a process of forming a polymeric  
structure, such as a coating, film, or solid body,  
15 comprising forming the aforementioned composition of  
one or more compounds of formula (1) and a  
photoinitiator, and then irradiating the composition  
with ultraviolet or electron beam radiation effective  
to polymerize said one or more compounds of formula  
20 (1).

Referring to formula (1), it can be seen  
that R represents a linear, branched or cyclic alkyl  
group having at least two substituents and as many as  
four substituents, one of which is a R<sup>2</sup> group and up  
25 to (n) of which have the formula -OCH=CH-CH<sub>2</sub>R<sup>1</sup>. As  
will be described below, up to (n-1) substituents can  
have the formula -OCH<sub>2</sub>CH=CHR<sup>1</sup> instead of -OCH=CHCHR<sup>1</sup>.  
Preferred R groups include the branched structures  
having the formula CH<sub>3</sub>C(CH<sub>2</sub>-)<sub>3</sub>, or C(CH<sub>2</sub>-)<sub>4</sub>.

30

35

Referring again to formula (1), it can be  
1 seen that the  $R^2$  substituent always contains an oxygen  
atom which is also bonded to the R group. Thus,  $R^2$   
can be hydroxyl, in which case the resulting compound  
is referred to herein as "underivatized".  
5 Alternatively,  $R^2$  can be alkoxy containing 1 to 20  
carbon atoms, phenoxy, acryloyloxy, methacryloyloxy,  
or any of the acyloxy, acyloxycarbonyloxy, or urethane  
derivatives represented by the formula  $A-(Het)_{0-1}-$   
C(O)O- wherein A is alkyl containing 1 to 20 carbon  
10 atoms, and (Het) represents the optional oxygen or NH-  
atoms. When  $R^2$  is alkoxy it can optionally be  
substituted with phenyl, thereby creating for example  
a benzyloxy substituent. When  $R^2$  is alkoxy containing  
two or more carbon atoms, two consecutive carbon atoms  
15 thereof can optionally be joined with an oxygen atom  
to form an epoxy ring. The embodiments wherein  $R^2$  is  
other than hydroxyl are at times referred to herein as  
the derivatized embodiments of the compounds of the  
present invention.  
20 It can also be seen in the definition of  
formula (1) that  $R^2$  can be a substituent of the  
formula  $-L-X-(L-R-(OCH=CH-CH_2R^1)_n)_i$ . In these  
embodiments, a central moiety X is substituted with a  
total of (i+1) substituents of the formula  
25  $(-L-R-(OCH=CH-CH_2R^1)_n)$ . Suitable X groups include, but  
are not limited to -Ph- groups, wherein -Ph- is  
phenylene (i.e. 1,2-phenylene, 1,3-phenylene, or 1,4-  
phenylene), as well as -Ph-Ph-;

30

35

1        $\text{-Ph}_{0.1}\text{-C}_a\text{H}_{2s}\text{-Ph}_{0.1}$  groups in which  $\text{C}_a\text{H}_{2a}$  is an alkylene  
group containing 1 to 20 carbon atoms; and groups  
consisting of a  $\text{C}_f\text{H}_{2f}$  and a  $\text{C}_g\text{H}_{2g}$  moiety which are  
bonded to  $\text{-C(O)-}$ ,  $\text{-O-}$ ,  $\text{-C(O)O-}$ ,  $\text{-Ph-}$  or  $\text{-C(O)NH-}$  and f  
and g are each 1 to 12. The  $\text{C}_a\text{H}_{2a}$ ,  $\text{C}_f\text{H}_{2f}$  and  $\text{C}_g\text{H}_{2g}$  groups  
5       can be straight or branched, and they can be attached  
to adjacent moieties at the same carbon atom (e.g.  
 $\text{-CH}_2\text{-}$ ,  $\text{CH}_3\text{CCH}_3$ ) or at different carbon atoms (e.g.  
 $\text{-CH}_2\text{CH}_2\text{-}$ ,  $\text{-CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{-}$ ).

10       In formula (1), L represents a linking group  
between the X moiety in each of the substituted R  
groups. Suitable linking groups L include a single  
chemical bond,  $\text{-C(O)O-}$ ,  $\text{-OC(O)O-}$ ,  $\text{-O-}$ , and  $\text{-NHC(O)O-}$   
bearing in mind that in any case each R group is  
bonded to an oxygen atom of the linking group L.  
15       Also, when L is a chemical bond, X can be  $\text{-C(O)-}$ .

Specific preferred examples of compounds in  
accordance with this description are provided  
hereinbelow.

20       The choice of routes for synthesizing the  
compounds of the present invention is dictated  
principally by the particular target compound desired.  
As will be seen below, in many cases there are several  
different routes available to synthesize a particular  
compound.

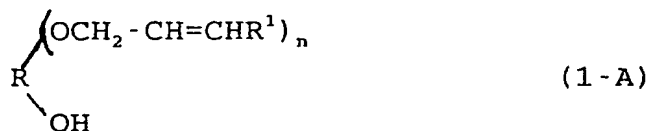
25       To synthesize those embodiments of the  
present invention wherein  $\text{R}^2$  is  $\text{-OH}$ , the preferred  
route is isomerization of the allyl ether analog of

30

35

- 6 -

the desired propenyl compound. Those allyl ether  
 1 analogs thus have the formula (1-A)



5 wherein R, R<sub>1</sub> and n are as defined herein. This allyl precursor, if not available commercially, can be prepared by reacting a precursor of formula R(OH)<sub>n+1</sub> with an appropriate number of moles of an allyl  
 10 chloride of the formula Cl-CH<sub>2</sub>-CH=CHR<sup>1</sup> (or the corresponding bromide) calculated to provide the desired hydroxyl substituted compound of formula (1-A).

The allyl ether precursor of formula (1-A)  
 15 is converted to the desired propenyl product by isomerization of the allyl compound. This isomerization is carried out in the presence of a small but effective amount of a catalyst for the isomerization, in the presence or absence of a solvent  
 20 which is inert to the reactant, product and catalyst. Catalysts for the isomerization include strong bases, such as potassium t-butoxide-DMSO, and sodium amide. Other suitable catalysts for this isomerization include transition metal-containing catalysts, such as  
 25 tris(triphenylphosphine) ruthenium (II) dichloride, tris(triphenylphosphine) rhodium (I) chloride, ruthenium on alumina, and iron pentacarbonyl.

While complete isomerization of all allyl groups present to propenyl is preferred, it is also  
 30



- 7 -

1 contemplated that some but not all allyl groups  
isomerize to propenyl.

Compounds of formula (I) wherein  $R^2$  is  
alkoxy, phenoxy, acryloyloxy, methacryloyloxy, or A-  
(Het)<sub>0-1</sub>-C(O)O- can be synthesized in either of two  
5 ways. One way involves the formation of the propenyl-  
substituted compound as described above wherein  $R^2$  is  
hydroxyl, followed by derivatization of the hydroxyl-  
substituent by reaction thereof with a suitable  
reagent by which the desired  $R^2$  group replaces the  
10 hydroxyl group. For instance, when the desired  $R^2$   
group is alkoxy, the corresponding hydroxyl-  
substituted compound can be reacted with the  
corresponding alkyl halide, such as alkyl bromide,  
under alkaline conditions. When the desired  $R^2$  group  
15 is phenoxy; the hydroxyl-substituted compound of  
formula (1) can be reacted with p-toluene sulfonyl  
chloride to form an intermediate tosylate ester, which  
is then reacted with phenol to form the desired  
phenoxy compound. Acyloxy derivatives such as  
20 acryloyloxy, methacryloyloxy, A-O-C(O)O- and A-C(O)O-  
derivatives can be formed by reacting the  
corresponding acyl chloride or anhydride with the  
compound of formula (1) wherein  $R^2$  is -OH. The  
urethane derivatives, of the formula A-NH-C(O)O- can  
25 be formed by reacting the corresponding isocyanate  
with a compound of formula wherein  $R^2$  is -OH.

Another route for synthesizing compounds of  
formula (1) involves first reacting the allyl ether  
precursor having formula (1-A) to derivatize the  
30

- 8 -

hydroxyl group by employing any of the procedures  
1 available for derivatizing the hydroxyl-substituted  
propenyl compound, so as to form a suitably  
derivatized allyl compound, and then isomerizing the  
derivatized allyl compound to the desired propenyl  
5 product. The isomerization conditions and catalysts  
suitable for the isomerization are the same as  
described hereinabove with respect to isomerization of  
compounds of formula (1-A).

To produce compounds of the formula (1)  
10 wherein the  $R^2$  substituent contains a linking group L  
as defined hereinabove, it is preferred first to react  
the allyl analog wherein  $R^2$  is hydroxyl, with a  
compound corresponding to the formula  $X-(L-Z)_{i+1}$ . For  
this reactant, X is as defined above and the linking  
15 groups L are as defined hereinabove. The terminal  
group Z is any capping group which will leave the L  
group (or, when L is a chemical bond, leave the X  
group) upon reaction with the hydroxyl-substituted  
allyl reactant so as to permit formation of the  
20 desired linkage between the L groups and R groups.  
For instance, when the L groups are to be ester  
linkages between the X group and the respective R  
moieties, the group Z can be hydrogen or lower alkyl  
such that the reaction between the precursor  $X(-L-Z)_{i+1}$   
25 is a matter of esterification or transesterification.  
Other routes and suitable reactants permitting the  
incorporation of other L linking groups disclosed  
herein will be apparent to those of ordinary skill in  
this art.

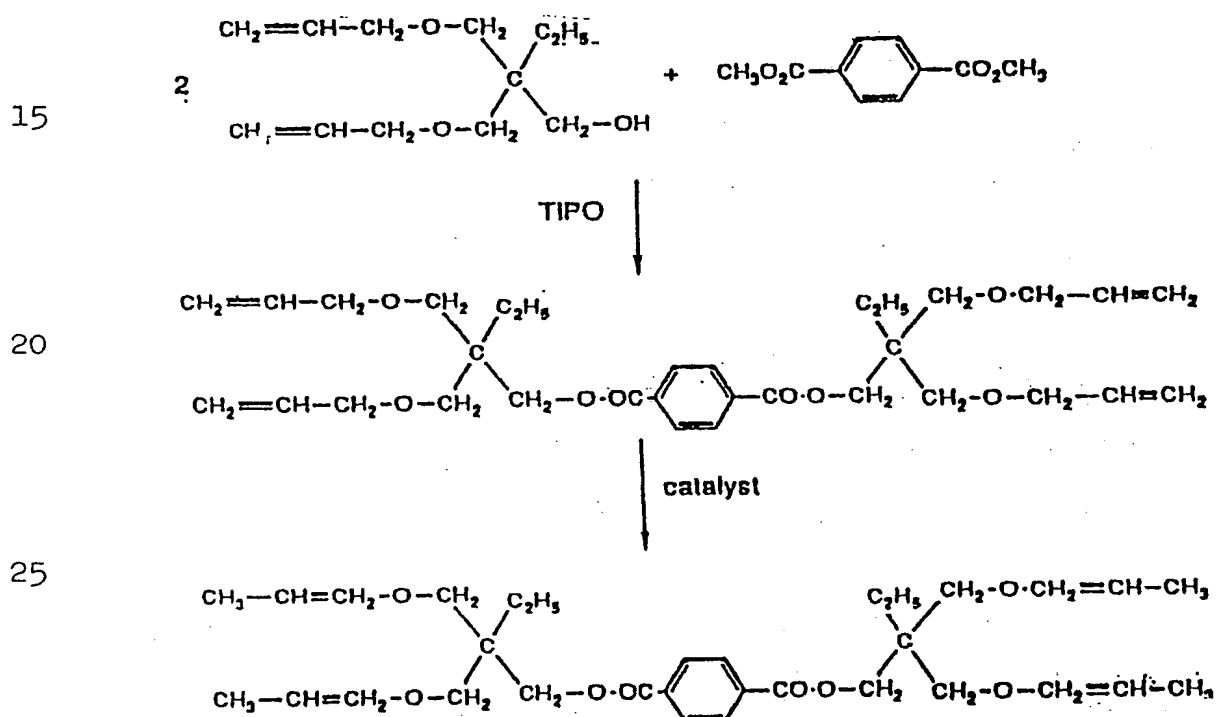
30

35

Following formation of the intermediate allyl analog in this manner, the intermediate is isomerized in the presence of any of the isomerization catalysts described hereinabove to form the product propenyl derivative having a plurality of propenyloxy groups attached to the X moiety through the R moiety and the L linking groups.

One example of the synthesis of such a multifunctional compound is the following: (termed herein Scheme A):

10



-10-

Analogous compound where the 1,4-phenylene  
1 is replaced by linear, branched or cyclic alkylene, or  
by other position isomers of phenylene, can be made by  
the same procedure from the appropriate diester.

Compounds containing -C(O)- in place of the  
5 - (O)CC<sub>6</sub>H<sub>4</sub>C(O)- moiety in Scheme A can be prepared by an  
analogous procedure from the diallyl precursor and  
diethyl carbonate in the presence of TIPO, (titanium  
tetra-isopropoxide) to form the allyl analog of the  
desired final product, followed by catalytic  
10 isomerization of the allyl groups to propenyl.

Compounds containing phenylene or straight,  
branched or cyclic alkylene in place of the -  
(O)CC<sub>6</sub>H<sub>4</sub>C(O)- moiety on Scheme A can be prepared by  
reacting the diallyl precursor and X-(hal)<sub>2</sub>, wherein  
15 hal is chlorine, bromine or iodine, in the presence of  
e.g. NaOH or KOH, to form the allyl analog of the  
desired final product, followed by catalytic  
isomerization of the allyl groups to propenyl.

Compounds containing a - (O)CNH-X-NHC(O)  
20 linkage in place of the - (O)CC<sub>6</sub>H<sub>4</sub>C(O)- moiety in Scheme  
A can be prepared by reacting the diallyl precursor  
with the polyisocyanate X(NCO)<sub>4</sub> in the presence of  
e.g. stannous octoate to form the analog of the  
desired final product, followed by catalytic  
25 isomerization of the allyl groups to propenyl.

Compounds containing a - (O)CO-X-OC(O)-  
linkage in place of the - (O)CC<sub>6</sub>H<sub>4</sub>C(O)- moiety in Scheme  
A can be prepared by reacting the diallyl precursor  
with X(OC(O)Cl)<sub>4</sub> in the presence of e.g. tributylamine  
30

-11-

1 to form the allyl analog of the desired final product,  
followed by catalytic isomerization of the allyl  
groups to propenyl.

5 The propenyl compounds of formula (1) are  
readily polymerized by exposure to ultraviolet or  
electron beam radiation in the presence of a cationic  
photoinitiator. Among those photoinitiators which may  
be used to achieve polymerization are diazonium salts,  
diaryliodonium salts, triarylsulfonium salts,  
diaryliodosonium salts, triarylsulfoxonium salts,  
10 dialkylphenacylsulfonium salts, and dialkyl-4-  
hydroxyphenylsulfonium salts. Typically, these salts  
contain complex metal halide or other non-nucleophilic  
ions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  
( $\text{C}_6\text{F}_5$ ) $_4\text{B}^+$  and the like. Examples of suitable  
15 photoinitiator salts are described hereinbelow and  
include those described in Crivello and Dietliker, in  
Chemistry & Technology of UV & EB Formulation For  
Coatings, Inks & Paints, Vol. 3, 1991, page 329, the  
disclosure of which is hereby incorporated herein by  
20 reference.

The amount of photoinitiator should be in  
the range of about 0.1 to 10% by weight based on the  
weight of the compound or compounds of formula (1).  
As noted herein, the compositions containing compounds  
25 of formula (1) and one or more photoinitiators for  
polymerization of such compounds comprises one aspect  
of the present invention.

Rapid and complete polymerization of the  
compounds of formula (1) can be achieved by  
30

35

-12-

irradiating the composition with an electron beam dose  
1 on the order of 0.1 to 10 Mrad or ultraviolet  
radiation flux on the order of 10-30 mW/cm<sup>2</sup>. Higher  
energy levels are also useful, especially when higher  
throughput speeds are desired or thicker masses of  
5 polymer are presented.

Photopolymerizable compositions containing  
the compounds for formula (I) can also contain any of  
the other additives customary for such uses, in the  
amounts thereof adequate to enable the additive to  
10 perform its desired function. Such additives include  
photosensitizers, fillers, flow control agents and the  
like. Examples of suitable materials for providing  
these functions abound in this field and are well  
known to those experienced in this field, and include  
15 the materials which are employed for those functions  
with other radiation-curable monomers such as  
acrylates and vinyl ethers. In addition, other  
comonomers may be present such as epoxies, vinyl  
ethers and 1-butenyl ethers.

20 Films and coatings formed by irradiation of  
compositions containing any of the compounds of  
formula (I) exhibit satisfactory and even superior  
mechanical strength, adhesion to substrate, high  
temperature stability, and high reactivity. It is not  
25 necessary to formulate the photo-polymerizable or  
electron beam-polymerizable composition in a solvent,  
thus permitting the operator to avoid the hazards and  
inconvenience of using solvents.

30

35

The following Table 1 identifies particular  
1 R<sup>2</sup> substituents which are referred to in the following  
examples and discussion:

5

Table 1

10	Substituent No.	Substituent
	1	OCH <sub>3</sub>
	2	OC <sub>4</sub> H <sub>9</sub>
	3	OC <sub>8</sub> H <sub>17</sub>
	4	OC <sub>6</sub> H <sub>5</sub>
15	5	OC (O) CH <sub>3</sub>
	6	OC (O) CH=CH <sub>2</sub>
	7	OC (O) OC <sub>4</sub> H <sub>9</sub>
	8	OC (O) NHC <sub>4</sub> H <sub>9</sub>
20	9	OC (O) NHC <sub>6</sub> H <sub>5</sub>

25

30

35

1           In the following Examples, derivatives of  
trimethylolpropane diallyl ether and of  
trimethylolpropane dipropenyl ether were prepared.  
The diallyl ether derivatives are identified with the  
number of the substituents in the R<sup>2</sup> position followed  
5 by the letter A, and dipropenyl ether derivatives are  
identified with the number of the substituent in the  
R<sup>2</sup> position followed by the letter P.

10

15

20

25

30

35



-15-

Examples

1

<sup>1</sup>H-NMR spectra were recorded either on a Varian XL-200 MHz or Unity 500 MHz spectrometer at room temperature in CDCl<sub>3</sub>. Elemental analyses were performed by Atlantic Microlabs Inc, Norcross, GA. Routine infrared spectra were obtained on a Midac FT-IR. Real-time IR were recorded on a Midac FT-IR (Midac Corp., Irvine, CA) equipped with a liquid nitrogen cooled MCT-detector at a scan rate of 270 scans per minute and a resolution of 4 cm<sup>-1</sup>. The data was recorded using the software program LabCalc (Galactic Software, Salem CT) and processed with Grams/386 (Galactic Software, Salem CT). The FT-IR was equipped with a UVEXS Co. Model SCU 110 UV lamp fitted with a fiber optical cable. The UV radiation flux on the sample was 17-18 mW/cm<sup>2</sup>.

Trimethylolpropane Di(1-propenyl) methyl ether (1P)

20

Trimethylolpropane diallyl ether (20 g, 93 mmol), 14.1 g (112 mmol) of dimethyl sulfate, 4.48 g (112 mmol) of powdered sodium hydroxide and 50 mL of toluene were combined in a three neck round bottom flask equipped with a thermometer, overhead stirrer and a reflux condenser. The suspension was stirred for 10 minutes at 40°C. Tetra-n-butylammonium bromide (0.2 g) were added and the suspension was heated to 110°C for 6 hours. The solution was cooled to room temperature, extracted with a 1 M sodium hydroxide

30

35

-16-

1 solution, washed three times with water and the  
solvent was evaporated. The residue was subjected to  
fractional distillation under reduced pressure (b.p.  
55°C/0.3 mm, Yield: 19.4 g; 91%).

5 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ(ppm) 0.84 (t, 3H), 1.42 (quart., 2H),  
3.28 (s, 2H), 3.34 (s, 7H), 3.96 (d, 4H), 5.16 (d, 2H),  
5.25 (d, 2H), 5.89 (m, 2H)

10 Allyl ether 1A (17 g, 74 mmol) and 0.02 g (22  
μmol) of tris(triphenylphosphine)ruthenium (II)  
dichloride were heated under nitrogen for 1 hour to  
160°C. The propenyl ether 1P was distilled under  
reduced pressure (b.p. 48°C/0.25mm; Yield: 16.7 g,  
98%).

15 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ=0.84 (m, 3H), 1.42 (m, 2H), 1.56  
(d, 3H, CH<sub>3</sub> trans-propenyl ether), 1.59 (d, 3H, CH<sub>3</sub> cis-  
propenyl ether), 3.28 (s, 2H), 3.35 (s, 3H), 3.52 (s, 2H,  
trans-propenyl ether), 3.62 (s, 2H, cis-propenyl ether),  
20 4.33 (m, 1H, cis-propenyl ether), 4.78 (m, 1H, cis-  
propenyl ether), 5.95 (m, 1H, cis-propenyl ether), 6.21  
(d, 1H, trans-propenyl ether)

25 Elemental Analysis: Calculated for C<sub>13</sub>H<sub>24</sub>O<sub>3</sub>, C,  
68.38 %, H, 10.59%.  
Found C: 68.36%; H, 10.55%

Synthesis of Trimethylolpropane Di(1-propenyl) Butyl  
(2A) and Octyl (3A) Ethers

30

35

-17-

Trimethylolpropane diallyl ether (10 g, 46.7 mmol), 93.3 mmol of n-butyl or n-octyl bromide, 15.7g of potassium hydroxide and 90 mL of DMSO were stirred for two hours at room temperature. The solution was diluted with 200 mL of water and extracted twice with 50 mL of ethyl acetate. The combined organic phases were washed with water and then dried over anhydrous sodium sulfate. After evaporation of the solvent, the residue was distilled under reduced pressure yielding 67% 2A (b.p. 110°C/0.1mm).

10

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$ (ppm)=0.84 (m,6H), 1.35 (quint.,2H), 1.42 (quart.,2H), 1.57 (quint.,2H), 3.28 (s,2H), 3.34 (s,4H), 3.40 (t,2H), 3.96 (d,4H), 5.16 (d,2H), 5.25 (d,2H), 5.89 (m,2H)

15

In a similar fashion, 3A (b.p.145°C/0.05 mm) was prepared in 56% yield.

20

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta$ (ppm)=0.84 (m,6H), 1.25-1.36 (m,8H), 1.42 (quart., 2H), 1.53 (quint.,2H), 3.28 (s,2H), 3.32 (s,4H), 3.39 (t,2H), 3.96 (d,4H), 5.16 (d,2H), 5.25 (d,2H), 5.89 (m,2H)

25

Both of the allyl ethers 2A and 3A were isomerized completely by heating at 170°C for 1 hour with 0.02 g (22  $\mu\text{mol}$ ) of tris(triphenylphosphine)ruthenium(II)dichloride as the catalyst.

30

35

-18-

Trimethylolpropane di(1-propenyl) n-butyl  
1 ether 2P (b.p. 113°C/0.2mm) was obtained in a 95%  
yield.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ(ppm)=0.82-0.90 (m,6H), 1.38 (m,2H)  
5 1.38-1.59 (m,12H), 3.28 (s,2H), 3.39 (t,2H), 3.55  
(s,2H,trans-propenyl ether), 3.64 (s,2H,cis-propenyl  
ether), 4.33 (m,1H,cis-propenyl ether), 4.78 (m,1H  
trans-propenyl ether), 5.95 (m,1H,cis-propenyl ether),  
10 6.12 (d,1H,trans-propenyl ether)

Elemental Analysis: Calculated for C<sub>16</sub>H<sub>30</sub>O<sub>3</sub>:C, 73.57%;  
H:11.73%.

Found: C, 73.63%; H, 11.70%.

15 Trimethylolpropane di(1-propenyl)n-octyl  
ether 3P was obtained in 98% yield (b.p. 155°C/0.1  
mm).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ(ppm)=0.80-0.91 (m,6H), 1.22-1.61  
20 (m,22H) 3.30 (s,2H), 3.39 (m,2H), 3.55 (s, 2H, trans-  
propenyl ether), 3.64 (s,2H, cis-propenyl ether), 4.33  
(m,1H, cis-propenyl ether), 4.78 (m,1H, trans-propenyl  
ether), 5.95 (m,1H, cis-propenyl ether), 6.12 (d,1H,  
trans-propenyl ether)

25 Elemental Analysis: Calculated for C<sub>20</sub>H<sub>38</sub>O<sub>3</sub>:C, 73.57%;  
H, 11.73%

Found: C, 73.63%; H, 11.70%.

30

35

-19-

1      Synthesis of Trimethylolpropane Di(1-propenyl) phenyl  
Ether (4A)

Trimethylolpropane diallyl ether (30 g, 140 mmol), 50 mL of pyridine and 50 mL of toluene were combined in a two neck flask. The solution was heated  
5      to 60°C and 38.13 g (200 mmol) p-toluenesulfonyl chloride dissolved in 100 mL of chloroform were added dropwise over a period of 1 hour. The solution was stirred at 60°C for an additional three hours. After cooling to room temperature, the solution was  
10     extracted with saturated sodium bicarbonate solution until no more carbon dioxide was evolved. After washing three times with water, the solvent was evaporated and the crude product used for further reactions. The yield of trimethylolpropane diallyl  
15     ether tosylate ester was 46.1 g (89%).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ(ppm) 0.79 ppm (t, 3H), 1.39 (quart., 2H)  
2.42 (s, 3H), 3.22 (s, 4H), 3.83 (d, 4H), 3.96 (s, 2H),  
5.14 (d, 2H), 5.19 (d, 2H), 5.89 (m, 2H), 7.32 (d, 2H),  
20     7.78 (d, 2H)

Elemental Analysis: Calculated for C<sub>19</sub>H<sub>28</sub>O<sub>5</sub>: C, 61.93%; H, 7.66%.

Found: C, 61.77%; H, 7.61%

Potassium tert-butoxide (3.04 g, 27.1 mmol) were dissolved in 30 mL of DMSO. Phenol (2.55 g, 27.1 mmol) was added and the solution heated under nitrogen to 70°C. There were added 5 g (13.57 mmol) of  
30

35

-20-

1 trimethylolpropane diallyl ether tosylate and the dark  
solution was stirred at 70°C for 6 hours. After  
cooling, the solution was diluted with 70 mL water and  
then extracted twice with 60 mL ethyl acetate. The  
5 combined organic extracts were washed three times with  
50 mL portions of water, dried over Na<sub>2</sub>SO<sub>4</sub> and the  
solvent removed by evaporation. The residue was  
distilled under reduced pressure (0.1 mm) at 150°C to  
give 2.01 g (51%) of colorless liquid 4A.

10 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ = 0.90 ppm (t, 3H), 1.57 (quart., 2H) 3.42  
(s, 4H), 3.88 (s, 2H), 3.96 (d, 4H), 5.16 (d, 2H), 5.25  
(d, 2H), 5.89 (m, 2H), 6.91 (m, 3H), 7.24 (m, 2H)

The allyl ether was quantitatively  
15 isomerized at 175°C for 1 hour with 0.02 g (22 μmol)  
of tris(triphenylphosphine)ruthenium (II) dichloride  
as the catalyst. The yield of 4P (b.p. 155°C/0.2 mm)  
was 97%.

20 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ (ppm) 0.90 (m, 3H), 1.50-1.64 (m, 8H),  
3.65 (d, 2H, trans-propenyl ether), 3.78 (d, 2H, cis-  
propenyl ether), 3.88 (t, 2H), 4.37 (m, 1H, cis-propenyl  
ether), 4.78 (m, 1H, trans-propenyl ether), 5.95 (m, 1H,  
cis-propenyl ether), 6.22 (d, 1H, trans-propenyl ether),  
25 6.91 (m, 3H), 7.24 (m, 2H)

Elemental Analysis: Calculated for C<sub>18</sub>H<sub>26</sub>O<sub>3</sub>:  
C, 74.45%; H, 9.02 %.

Found: C, 74.55%; H, 9.02%

30

35

- 21 -

1        Synthesis of Trimethylolpropane Di(1-propenyl)ether  
Acetate(5P)

5                Trimethylolpropane diallyl ether (20 g, 93.3  
mmol) and 12.4 mL (121 mmol) of acetic anhydride were  
dissolved in 40 mL of toluene. One drop of pyridine  
was added and the solution heated to reflux for 16 h.  
After cooling, the solution was extracted with  
saturated sodium bicarbonate solution until no more  
gas was evolved. The solution was washed with water,  
10        and the organic layer separated and dried over  
anhydrous sodium sulfate. The solvent was removed on  
a rotary evaporator and the residue distilled under  
reduced pressure. The fraction boiling at 76°C/0.025  
mm was collected. The yield of 5A was 22.7 g (95%).

15                <sup>1</sup>H-NMR (CDCl<sub>3</sub>):δ(ppm) 0.83 (t,3H), 1.43 (quart.,2H),  
2.05 (s,3H), 3.33 (s,4H), 3.93 (d,4H), 4.03 (s,2H),  
5.15 (d,2H), 5.24 (d,2H), 5.87 (m,2H)

20                The isomerization of 5A to 5P was conducted  
with tris(triphenylphosphine)ruthenium (II) dichloride  
as the catalyst at 190°C under N<sub>2</sub>. After 20 minutes  
the conversion to the propenyl ether 5P was complete  
as determined by <sup>1</sup>H-NMR. The product was purified by  
25        fractional vacuum distillation to yield compound 5P in  
97% overall yield (b.p. 82°C/0.05 mm).

30                <sup>1</sup>H-NMR (CDCl<sub>3</sub>):δ(ppm) 0.87 (m,3H), 1.46 (m,2H), 1.53-  
1.59 (m,6H), 2.06 (s,3H), 3.57 (d,2H,trans-propenyl

-22-

ether), 3.63 (d, 2H, cis-propenyl ether), 4.02 (t, 2H),  
1 4.37 (m, 1H, cis-propenyl ether), 4.77 (m, 1H, trans-  
propenyl ether), 5.91 (m, 1H, cis-propenyl ether), 6.21  
(d, 1H, trans-propenyl ether)

5 Elemental Analysis: Calculated for  $C_{14}H_{24}O_4$ : C, 65.60%;  
H, 9.44%  
Found: C, 65.49%; H, 9.48%

10 Preparation of Trimethylolpropane Di(1-propenyl) Ether  
Acrylate (6P)

There were combined 10 g (47 mmol) of  
trimethylolpropane diallyl ether, 30 g (0.234 mol) of  
n-butyl acrylate and 0.5 g of titanium (IV) tetra  
15 isopropoxide (TIPO) was added. The solution was  
stirred under nitrogen at 150°C for 10 hours. After  
this time, the solvent and the excess n-butyl acrylate  
were removed by distillation under reduced pressure.  
The fraction boiling at 112°C/0.05 mm was collected.  
20 The yield of 6A was 7.06 g (56%).

$^1H$ -NMR ( $CDCl_3$ ):  $\delta$ (ppm) 0.87 (t, 3H), 1.43 (quart., 2H),  
3.36 (s, 4H), 3.92 (d, 4H), 4.12 (s, 2H), 5.15 (d, 2H),  
5.22 (d, 2H), 5.79-5.89 (m, 3H), 6.12 (m, 1H), 6.39  
25 (d, 1H)

Elemental Analysis: Calculated for  $C_{15}H_{24}O_4$ : C, 67.14%;  
H, 9.01%.  
Found: C, 67.21%; H, 9.12%.

30

35



- Allyl ether 6A was quantitatively isomerized  
1 as described in the previous examples by heating for  
20 minutes at 190°C under nitrogen. The conversion  
was complete after 25 minutes. The distilled product  
was extremely sensitive to air and polymerization took  
5 place upon exposure to air. Attempts to stabilize the  
compound by adding such free radical inhibitors as  
hydroquinone and tert.-butyl catechol also resulted in  
polymerization during the isomerization reaction.
- 10 <sup>1</sup>H-NMR (CDCl<sub>3</sub>): δ(ppm) 0.87 (m, 3H), 1.50 (m, 8H), 3.58  
(d, 2H), 3.65 (d, 2H), 4.15 (t, 2H), 4.38 (m, 1H, cis-  
propenyl ether), 4.77 (m, 1H, trans-propenyl ether),  
5.80-6.41 (m, 5H)
- 15 Preparation of 1-Propenyl Ether Substituted Urethanes  
8P and 9P

- Combined in a 100 mL round bottom flask  
equipped with a magnetic stirrer, reflux condenser and  
nitrogen inlet were 10 g (46.7 mmol) of  
20 trimethylolpropane diallyl ether and 61 mmol of either  
phenyl isocyanate or n-butyl isocyanate, then 0.01 g  
(0.15 mmol) of di-n-butyltin dilaurate were added.  
The solutions were stirred at room temperature for 30  
minutes and then heated to 60°C and stirred for an  
25 additional 30 minutes. After cooling, the products  
were purified by distillation in a Büchi  
microdistillation apparatus.
- 30
- 35

-24-

8A was obtained in 97% yield with a b.p. of  
1 180°C/0.1 mm.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>):δ(ppm) 0.85 (t,3H), 0.92 (t,3H), 1.32-  
1.50 (m,6H), 3.17 (m,2H), 3.30 (s,4H), 3.91 (d,4H),  
5 4.02 (s,2H), 5.13 (d,2H), 4.61 (s,1H, NH), 5.24  
(d,2H), 5.86 (m,2H).

9A was not distillable, and was purified by  
removing the starting isocyanate by heating in the  
10 microdistillation apparatus to 180°C for 1 h under  
high vacuum (0.05 mm). The yield was 94%.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>):δ(ppm) 0.87 (t,3H), 1.46 (quart.,2H),  
3.37 (s,4H), 3.96 (d,4H), 4.18 (s,2H), 5.16 (d,2H),  
15 5.25 (d,2H), 5.88 (m,2H), 6.60 (s,1H,NH), 7.05 (t,  
1H), 7.30-7.41 (m,4H).

Isomerizations of 8A and 9A were conducted with the  
ruthenium catalyst under nitrogen.

20

8A was isomerized to 8P in 8% yield after 2h  
at 180°C and purified by vacuum microdistillation  
(b.p. 182°C/0.1 mm).

25 <sup>1</sup>H-NMR (CDCl<sub>3</sub>):δ=0.80 - 0.95 ppm (m,6H), 1.30-1.60  
(m,12H), 3.18 (m,2H), 3.47 (d,2H, trans-propenyl  
ether), 3.62 (d,2H,cis-propenyl ether), 4.04 (d,2H),  
4.38 (m,1H,cis-propenyl ether), 4.62 (s,1H, NH), 4.78

30

35

-25-

(m, 1H, trans-propenyl ether), 5.93 (m, 1H, cis-propenyl  
1 ether), 6.21 (d, 1H, trans-propenyl ether)

Elemental Analysis: Calculated for  $C_{17}H_{31}NO_4$ : C, 65.14%;  
H, 9.97%; N, 4.47%.

5 Found: C, 65.89%; H, 10.18%; N, 4.05%.

9A was isomerized to 9P in 89% yield after  
2h at 180°C. Purification was accomplished by vacuum  
microdistillation (b.p. 190°C/0.025 mm).

10

$^1H$ -NMR ( $CDCl_3$ ):  $\delta$ =0.80 - 1 ppm (m, 6H), 1.45-1.70 (m, 8H),  
3.69-3.80 (m, 4H), 4.20 (d, 2H), 4.39 (m, 1H, cis-  
propenyl ether), 4.79 (m, 1H, trans-propenyl ether),  
5.92 (m, 1H, cis-propenyl ether), 6.22 (d, 1H, trans-  
15 propenyl ether), 6.81 (s, 1H, NH), 7.05 (t, 1H), 7.29-  
7.40 (m, 4H)

Elemental Analysis: Calculated for  $C_{19}H_{27}NO_4$ : C, 68.44%;  
H, 8.16%; N, 4.20%.

20 Found: C, 68.38%; H, 8.13%; N, 4.08%

#### UV Cure of Novel Monomers

Thin films (~25  $\mu$ m) of the liquid monomers  
25 containing 0.5 mol% of IOC10 ((4-n-decyloxyphenyl)  
phenyliodonium hexafluoroantimonate) photoinitiator  
were drawn onto glass or steel panels and irradiated  
using a GE H3T-7 200 W medium pressure mercury arc  
lamp mounted at a distance of 12 cm from the sample.

30

35

-26-

1 This apparatus was equipped with a mechanical shutter  
which could be opened to expose the samples to UV  
irradiation. With monomers 1P-7P, polymerization of  
the monomers took place within 0.5-1 second to give  
crosslinked solid films of the polymer. Monomer 8P  
5 did not polymerize under these conditions while longer  
irradiation times (1-2 minutes) were required to  
polymerize monomer 9P.

The polymerizations were also followed in  
detail by real-time infrared spectroscopy (RTIR), a  
10 method described by Decker and Moussa in J. Polym.  
Sci. Part a: Polym. chem., 28, 4329 (1990). For this  
solutions of the photoinitiator (IOC10) in a  
concentration of 0.5 mol% in the monomers were  
prepared. The solution was coated on a commercially  
15 available Saran® film (polyvinylidene chloride). The  
films were then covered by a second Saran film and  
this assembly mounted in conventional 5 x 5 cm slide  
frames. This sandwich was placed in a horizontally  
mounted Midac Corp. FT-IR spectrometer. The  
20 instrument was equipped with a UVEXS Co. Model SCU 110  
UV lamp fitted with a fiber optic cable and the probe  
of the fiber optic cable positioned so as to direct UV  
irradiation onto the sample window of the  
spectrometer. UV intensity was measured with the aid  
25 of a Control Cure Radiometer and found to be 18-19  
mW/cm<sup>2</sup>. To determine the rate of polymerization the  
IR band at 1660 to 1670 cm<sup>-1</sup> was followed. The  
conversion was calculated by integrating the areas of  
the peak at  $t_0$  and  $t_{end}$ . The initial slopes of the  
30

-27-

curves ( $R_p/[M]_0$ ) were determined and are considered to  
1 be a measure of the reactivity of the monomers. In  
these studies, the acrylate substituted monomer 6P was  
not included since it is too unstable to be measured  
under air without polymerizing by oxygen induction.  
5 The results of the measurements are displayed and  
summarized in Table 2.

The results show that the methyl ether  
substituted monomer 1P has the highest rate of  
polymerization. This is expected since it this  
10 monomer does not contain polar groups which could  
interfere with the propagating carbenium ions. In  
addition, the methyl ether group is relatively small,  
so that steric factors are also small. The n-butyl  
and n-octyl ethers (2P and 3P) undergo rather sluggish  
15 photopolymerizations with IOC10. The reason for the  
surprisingly low rates of polymerization is the  
limited solubility of the photoinitiator (IOC10) in  
these monomers. In contrast, when the polymerization  
is carried out using the much more soluble  
20 commercially available di(dodecylphenyl)iodonium  
hexafluoroantimonate (UV 9380C), both monomers  
polymerize very rapidly and to high conversions. The  
n-octyl ether, 3P, polymerizes with a higher  
conversion of the propenyl ether groups than the n-  
25 butyl ether 2P. One reason may be when the former  
monomer is polymerized a polymer which possesses a  
lower glass transition temperature is produced.

30

35

Monomer	Photoinitiator*	PI conc. (mol%)	Slope ( $R_p [M_0] (s^{-1})$ )	Conversion (300s) (%)
1P	IOC10	0.5	5.3	74
2P	IOC10	0.5	0.25	40
2P	UV9380C	0.5	2.0	67
3P	IOC10	0.5	0.7	64
3P	UV9380C	0.5	2.9	75
4P	IOC10	0.5	1.8	65
5P	IOC10	0.5	2.7	74
7P	IOC10	0.5	2.6	75
8P	IOC10	0.5	0	0
8P	IOC10	2.0	0	0
9P	IOC10	0.5	0.06	10
9P	IOC10	1.0	0.4	27
9P	IOC10	2.0	0.5	30

\* -IOC10 is (4-n-decyloxyphenyl)iodonium hexafluoroantimonate and UV 9380C is di(dodecylphenyl)phenyliodonium hexafluoroantimonate

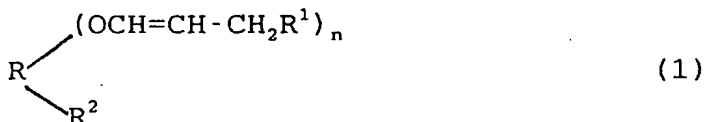
- 29 -

What Is Claimed Is:

1

1. A compound of the formula (1)

5



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl  
 10 containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon  
 atoms which is optionally substituted with phenyl and  
 two consecutive carbon atoms of which are optionally  
 15 bonded to an oxygen atom to form an epoxy ring,  
 phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>0.1</sub>-  
 C(O)O- wherein A is alkyl containing 1 to 20 carbon  
 atoms, and (Het) is -O- or -NH-;

or R<sup>2</sup> is -L-X-(L-R-(OCH=CH-CH<sub>2</sub>R<sup>1</sup>)<sub>n</sub>)<sub>i</sub> wherein  
 20 up to (n-1)-OCH=CH-CH<sub>2</sub>R<sub>1</sub> groups can instead be  
 -OCH<sub>2</sub>CH=CHR<sup>1</sup>;

wherein X has any of the structures -Ph<sub>0.1</sub>-C<sub>a</sub>H<sub>2a</sub>-Ph<sub>0.1</sub>-Ph<sub>0.1</sub>-(cyclo-C<sub>5-20</sub>-alkyl)-Ph<sub>0.1</sub>-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

25 -C<sub>f</sub>H<sub>2f</sub>C(O)C<sub>g</sub>H<sub>2g</sub> -C<sub>f</sub>H<sub>2f</sub>OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>C(O)OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>PhC<sub>g</sub>H<sub>2g</sub>-,  
 or -C<sub>f</sub>H<sub>2f</sub>C(O)NHC<sub>g</sub>H<sub>2g</sub>-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

provided that each R is bonded to an oxygen atom of L,

30

35

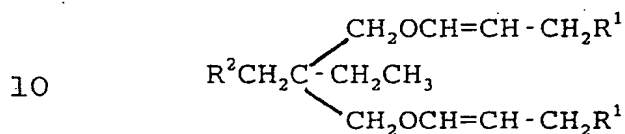
-30-

and i is an integer from 1 to 3; or X is -C(O)-, each  
 1 L is a chemical bond, and i is 1.

2. A compound according to claim 1 wherein  
 R<sup>1</sup> is -H.

5

3. A compound according to claim 1 of the  
 formula



4. A compound according to claim 1 of the  
 15 formula  
 $\text{R}^2-\text{CH}_2\text{C}(\text{CH}_2\text{OCH}=\text{CH}-\text{CH}_2\text{R}^1)_3$

5. A compound according to claim 1 wherein  
 R<sup>2</sup> is -OCH<sub>3</sub>, -OC<sub>4</sub>H<sub>9</sub>, -OC<sub>8</sub>H<sub>17</sub>, -OC<sub>6</sub>H<sub>5</sub>, -OC(O)CH<sub>3</sub>,  
 20 -OC(O)CH=CH<sub>2</sub>, -OC(O)OC<sub>4</sub>H<sub>9</sub>, -OC(O)NHC<sub>4</sub>H<sub>9</sub> or -OC(O)NH-C<sub>6</sub>H<sub>5</sub>.

6. A compound according to claim 1 wherein  
 R<sup>1</sup> is -H and R<sup>2</sup> is -OC(O)-C<sub>6</sub>H<sub>4</sub>-C(O)O-R-(OCH=CHCH<sub>3</sub>)<sub>2</sub>.

25 7. A composition comprising a compound  
 according to claim 1 and an effective amount of a  
 photoinitiator for radiation-induced polymerization  
 thereof.

30

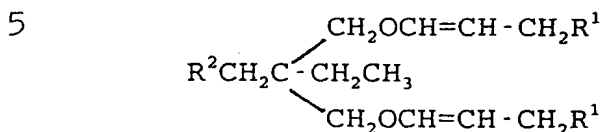
35



- 31 -

8. A composition according to claim 7  
 1 wherein  $R^1$  is -H.

9. A composition according to claim 7  
 wherein said compound has the formula



10. A composition according to claim 7  
 10 wherein said compound has the formula



11. A composition according to claim 7  
 15 wherein  $R^2$  is  $-OCH_3$ ,  $-OC_4H_9$ ,  $-OC_8H_{17}$ ,  $-OC_6H_5$ ,  $-OC(O)CH_3$ ,  
 $-OC(O)CH=CH_2$ ,  $-OC(O)OC_4H_9$ ,  $-OC(O)NHC_4H_9$  or  $-OC(O)NH-C_6H_5$ .

12. A composition according to claim 7  
 wherein  $R^1$  is -H and  $R^2$  is  $-OC(O)-C_6H_4-C(O)O-R-$   
 20  $(OCH=CHCH_3)_2$ .

13. A process for forming a polymer  
 comprising (a) forming a mixture comprising one or  
 more compounds according to claim 1 and at least one  
 25 cationic photoinitiator for polymerization of said  
 compound, and

(b) irradiating said mixture with  
 ultraviolet light or electron beam radiation of an

30

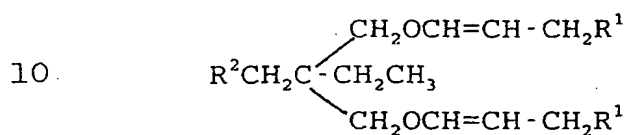
35

-32-

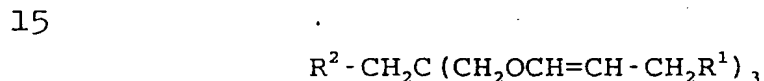
energy level, and for a time, sufficient to polymerize  
 1 said one or more compounds.

14. A process according to claim 13 wherein  
 5  $R^1$  is -H.

15. A process according to claim 13 wherein  
 said compound has the formula



16. A process according to claim 13 wherein  
 said compound has the formula



17. A process according to claim 13 wherein  
 $R^2$  is  $-OCH_3$ ,  $-OC_4H_9$ ,  $-OC_8H_{17}$ ,  $-OC_6H_5$ ,  $-OC(O)CH_3$ ,  
 20  $-OC(O)CH=CH_2$ ,  $-OC(O)OC_4H_9$ ,  $-OC(O)NHC_4H_9$  or  $-OC(O)NH-C_6H_5$ .

18. A process according to claim 13 wherein  
 $R^1$  is -H and  $R^2$  is  $-OC(O)-C_6H_4-C(O)O-R-(OCH=CHCH_3)_2$ .

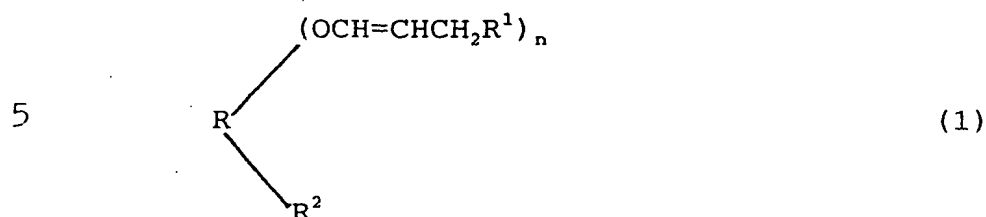
19. A product produced by the process of  
 any one of claims 13 to 18.

30

35

- 33 -

20. A process of making a compound of the  
 1 formula (1)



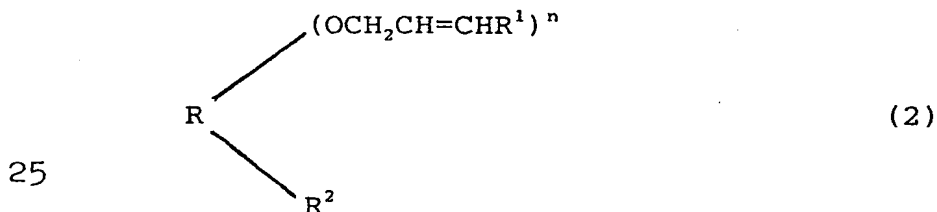
wherein n is an integer from 1 to 3;

10 R is linear, branched or cyclic alkyl  
 containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon  
 atoms which is optionally substituted with phenyl and  
 15 two consecutive carbon atoms of which are optionally  
 bonded to an oxygen atom to form an epoxy ring,  
 phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>0-1</sub>-  
 C(O)O- wherein A is alkyl containing 1 to 20 carbon  
 atoms, and (Het) is -O- or -NH-;

20 comprising isomerizing a compound of the formula (2)



to said compound of the formula (1) in the presence of  
 an effective amount of a catalyst for said  
 isomerization.

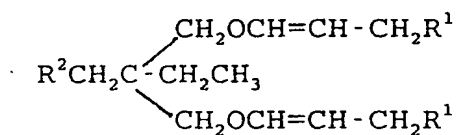
30

35

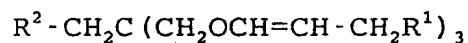
21. A process according to claim 20 wherein  
 1  $R^1$  is -H.

22. A process according to claim 20 wherein  
 said compound has the formula

5

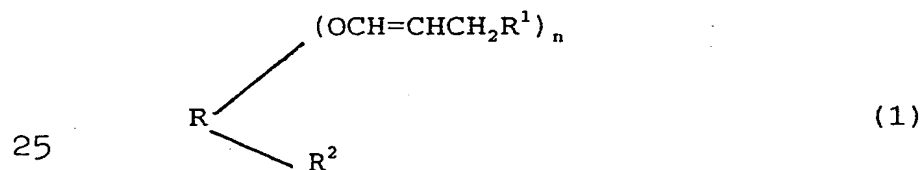


23. A process according to claim 20 wherein  
 said compound has the formula



24. A process according to claim 20 wherein  
 $R^2$  is  $-OCH_3$ ,  $-OC_4H_9$ ,  $-OC_8H_{17}$ ,  $-OC_6H_5$ ,  $-OC(O)CH_3$ ,  
 $-OC(O)CH=CH_2$ ,  $-OC(O)OC_4H_9$ ,  $-OC(O)NHC_4H_9$  or  $-OC(O)NH-C_6H_5$ .

25. A process of making a compound of the  
 formula (1)



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl  
 containing 1 to 6 carbon atoms;

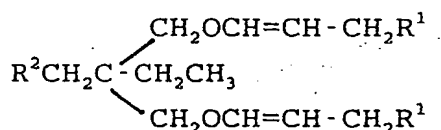
-35-

$R^1$  is -H or  $-CH_3$ ;

1  $R^2$  is alkoxy containing 1 to 20 carbon atoms  
 which is optionally substituted with phenyl and two  
 consecutive carbon atoms of which are optionally  
 bonded to an oxygen atom to form an epoxy ring,  
 5 phenoxy, acryloyloxy, methacryloyloxy, or  $A-(Het)_{0.1}-$   
 $C(O)O-$  wherein A is alkyl containing 1 to 20 carbon  
 atoms, and (Het) is -O- or -NH-;  
 comprising isomerizing an allyl compound of the  
 formula  $HO-R-(OCH_2CH=CHR^1)_n$  to a propenyl compound of  
 10 the formula  $HO-R-(OCH=CHCH_2R^1)$  in the presence of an  
 effective amount of a catalyst for said isomerization,  
 and then replacing the -OH group on said propenyl  
 compound with  $R^2$ .

15 26. A process according to claim 25 wherein  
 $R^1$  is -H.

20 27. A process according to claim 25 wherein  
 said compound has the formula



25 28. A process according to claim 25 wherein  
 said compound has the formula



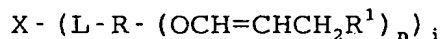
30

35

- 36 -

29. A process according to claim 25 wherein  
 1  $R^2$  is  $-\text{OCH}_3$ ,  $-\text{OC}_4\text{H}_9$ ,  $-\text{OC}_8\text{H}_{17}$ ,  $-\text{OC}_6\text{H}_5$ ,  $-\text{OC}(\text{O})\text{CH}_3$ ,  
 $-\text{OC}(\text{O})\text{CH}=\text{CH}_2$ ,  $-\text{OC}(\text{O})\text{OC}_4\text{H}_9$ ,  $-\text{OC}(\text{O})\text{NHC}_4\text{H}_9$  or  $-\text{OC}(\text{O})\text{NH}-\text{C}_6\text{H}_5$ .

30. A process of making a compound of the  
 5 formula



wherein  $n$  is an integer from 1 to 3;

10  $\text{R}$  is linear, branched or cyclic alkyl  
 containing 1 to 6 carbon atoms;

$\text{R}^1$  is  $-\text{H}$  or  $-\text{CH}_3$ ;

wherein  $\text{X}$  has any of the structures  $-\text{Ph}_{0.1}-\text{C}_a\text{H}_{2a}-\text{Ph}_{0.1}$   
 $-\text{Ph}_{0.1}-(\text{cyclo}-\text{C}_{5.20}-\text{alkyl})-\text{Ph}_{0.1}-$ ,  $-\text{Ph}-\text{Ph}-$ , or  $-\text{Ph}-$ ,

15 wherein  $\text{Ph}$  is phenylene and  $a$  is 1 to 20;

$-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{C}_g\text{H}_{2g}$ ,  $-\text{C}_f\text{H}_{2f}\text{OC}_g\text{H}_{2g}-$ ,  $-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{OC}_g\text{H}_{2g}-$ ,  $-\text{C}_f\text{H}_{2f}\text{PhC}_g\text{H}_{2g}-$ ,  
 or  $-\text{C}_f\text{H}_{2f}\text{C}(\text{O})\text{NHC}_g\text{H}_{2g}-$ , wherein  $f$  and  $g$  are each 1 to 12;

and each  $\text{L}$  is independently a chemical bond or

$-\text{C}(\text{O})\text{O}-$ ,  $-\text{OC}(\text{O})\text{O}-$ ,  $-\text{O}-$ , or  $-\text{NHC}(\text{O})\text{O}-$ ,

20 provided that each  $\text{R}$  is bonded to an oxygen atom of  $\text{L}$ ,  
 and  $i$  is an integer from 1 to 3; or  $\text{X}$  is  $-\text{C}(\text{O})-$ , each  
 $\text{L}$  is a chemical bond, and  $i$  is 1.

comprising reacting an allyl compound of the  
 formula  $\text{HO}-\text{R}-(\text{OCH}_2\text{CH}=\text{CHR}^1)_n$  with a compound containing  
 25 a moiety of the formula  $\text{X}-(\text{L}-)_{i+1}$ , to form an  
 intermediate of the formula  $\text{X}-(\text{L}-\text{R}-(\text{OCH}_2\text{CH}=\text{CHR}^1)_n)_{i+1}$   
 and then isomerizing said intermediate to said  
 compound of formula (1) in the presence of an  
 effective amount of a catalyst for said isomerization.

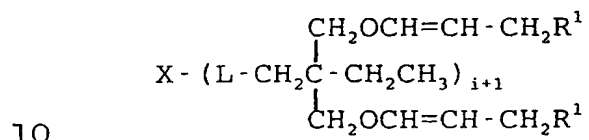
30

35

- 37 -

1                    31. A process according to claim 30 wherein  
                     R<sup>1</sup> is -H.

5                    32. A process according to claim 30 wherein  
                     said compound has the formula



                    33. A process according to claim 30 of the  
                     formula



15                    34. A process according to claim 30 wherein  
                     said compound has the formula  
                     (CH<sub>3</sub>CH=CHO)<sub>2</sub>-R-OC(O)-C<sub>6</sub>H<sub>4</sub>-C(O)O-R-(OCH=CHCH<sub>3</sub>)<sub>2</sub>!

20

25

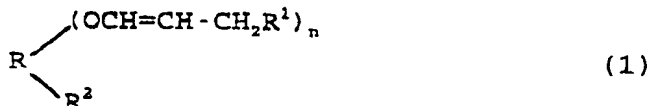
30

35

## AMENDED CLAIMS

[received by the International Bureau on 21 January 1999 (21.01.99);  
original claims 1-34 replaced by new claims 1-21 (7 pages)]

1. A compound of the formula (1)



10 wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl  
containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

15 R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon  
atoms which is optionally substituted with phenyl and  
two consecutive carbon atoms of which are optionally  
bonded to an oxygen atom to form an epoxy ring,  
phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>0.1</sub>-  
C(O)O- wherein A is alkyl containing 1 to 20 carbon  
20 atoms, and (Het) is -O- or -NH-;

or R<sup>2</sup> is -L-X-(L-R-(OCH=CH-CH<sub>2</sub>R<sup>1</sup>)<sub>n</sub>)<sub>i</sub> wherein  
up to (n-1)-OCH=CH-CH<sub>2</sub>R<sub>1</sub> groups can instead be  
-OCH<sub>2</sub>CH=CHR<sup>1</sup>;

wherein X has any of the structures -Ph<sub>0.1</sub>-C<sub>6</sub>H<sub>2a</sub>-Ph<sub>0.1</sub>

25 -Ph<sub>0.1</sub>-(cyclo-C<sub>5-20</sub>-alkyl)-Ph<sub>0.1</sub>-, -Ph-Ph-, or -Ph-,

wherein Ph is phenylene and a is 1 to 20;

-C<sub>f</sub>H<sub>2f</sub>C(O)C<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>C(O)OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>PhC<sub>g</sub>H<sub>2g</sub>-,  
or -C<sub>f</sub>H<sub>2f</sub>C(O)NHC<sub>g</sub>H<sub>2g</sub>-, wherein f and g are each 1 to 12;

and each L is independently a chemical bond or

30 -C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-,

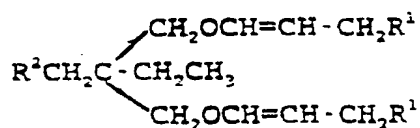


provided that each R is bonded to an oxygen atom of L, and i is an integer from 1 to 3; or X is -C(O)-, each L is a chemical bond, and i is 1.

5 2. A compound according to claim 1 wherein R<sup>1</sup> is -H.

3. A compound according to claim 1 of the formula

10



15 4. A compound according to claim 1 of the formula



20 5. A compound according to claim 1 wherein R<sup>2</sup> is -OCH<sub>3</sub>, -OC<sub>6</sub>H<sub>5</sub>, -OC<sub>8</sub>H<sub>17</sub>, -OC<sub>6</sub>H<sub>5</sub>, -OC(O)CH<sub>3</sub>, -OC(O)CH=CH<sub>2</sub>, -OC(O)OC<sub>6</sub>H<sub>5</sub>, -OC(O)NHC<sub>6</sub>H<sub>5</sub>, or -OC(O)NH-C<sub>6</sub>H<sub>5</sub>.

6. A compound according to claim 1 wherein R<sup>1</sup> is -H and R<sup>2</sup> is -OC(O)-C<sub>6</sub>H<sub>4</sub>-C(O)O-R-(OCH=CHCH<sub>3</sub>)<sub>2</sub>.

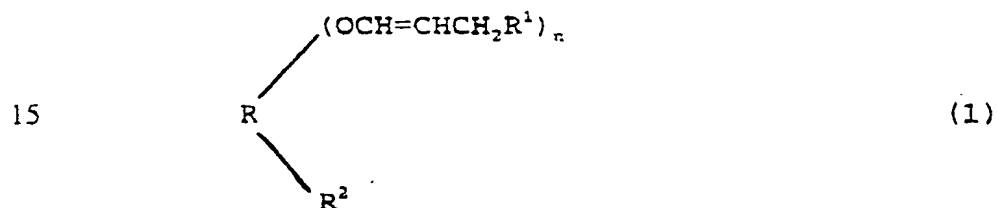
25

7. A composition comprising a compound according to any one of claims 1-6 and an effective amount of a photoinitiator for radiation-induced polymerization thereof.

30

8. A process for forming a polymer comprising (a) forming a mixture comprising one or more compounds according to claim 1 and at least one cationic photoinitiator for polymerization of said compound, and  
 5 (b) irradiating said mixture with ultraviolet light or electron beam radiation of an energy level, and for a time, sufficient to polymerize said one or more compounds.

10 9. A process of making a compound of the formula (1)



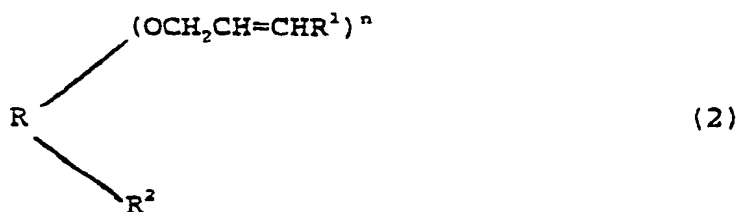
wherein n is an integer from 1 to 3;

20 R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

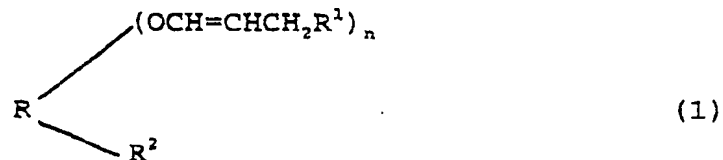
25 R<sup>2</sup> is -OH, alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>0-1</sub>-C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-;

30 comprising isomerizing a compound of the formula (2)



to said compound of the formula (1) in the presence of an effective amount of a catalyst for said isomerization.

10. A process of making a compound of the formula (1)



wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

R<sup>2</sup> is alkoxy containing 1 to 20 carbon atoms which is optionally substituted with phenyl and two consecutive carbon atoms of which are optionally bonded to an oxygen atom to form an epoxy ring, phenoxy, acryloyloxy, methacryloyloxy, or A-(Het)<sub>n-1</sub>-C(O)O- wherein A is alkyl containing 1 to 20 carbon atoms, and (Het) is -O- or -NH-;

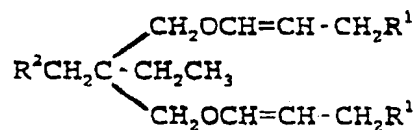
comprising isomerizing an allyl compound of the formula HO-R-(OCH<sub>2</sub>CH=CHR<sup>1</sup>)<sub>n</sub> to a propenyl compound of the formula HO-R-(OCH=CHCH<sub>2</sub>R<sup>1</sup>) in the presence of an effective amount

of a catalyst for said isomerization, and then replacing the -OH group on said propenyl compound with R<sup>2</sup>.

11. A process according to any one of claims 8-10 wherein R<sup>1</sup> is -H.

12. A process according to any one of claims 8-10 wherein said compound has the formula

10



13. A process according to any one of claims 8-10 wherein said compound has the formula



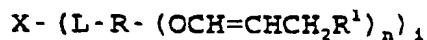
14. A process according to any one of claims 8 to 10 wherein R<sup>2</sup> is -OCH<sub>3</sub>, -OC<sub>4</sub>H<sub>9</sub>, -OC<sub>8</sub>H<sub>17</sub>, -OC<sub>6</sub>H<sub>5</sub>, -OC(O)CH<sub>3</sub>, -OC(O)CH=CH<sub>2</sub>, -OC(O)OC<sub>4</sub>H<sub>9</sub>, -OC(O)NHC<sub>4</sub>H<sub>9</sub> or -OC(O)NH-C<sub>6</sub>H<sub>5</sub>.

15. A process according to any one of claims 8-10 wherein R<sup>1</sup> is -H and R<sup>2</sup> is -OC(O)-C<sub>6</sub>H<sub>4</sub>-C(O)O-R-(OCH=CHCH<sub>3</sub>)<sub>2</sub>.

16. A product produced by the process of any one of claims 8 to 15.

30

17. A process of making a compound of the formula



5

wherein n is an integer from 1 to 3;

R is linear, branched or cyclic alkyl containing 1 to 6 carbon atoms;

R<sup>1</sup> is -H or -CH<sub>3</sub>;

10

wherein X has any of the structures -Ph<sub>0.1</sub>-C<sub>8</sub>H<sub>2a</sub>-Ph<sub>0.1</sub>, -Ph<sub>0.1</sub>-(cyclo-C<sub>5-20</sub>-alkyl)-Ph<sub>0.1</sub>-, -Ph-Ph-, or -Ph-, wherein Ph is phenylene and a is 1 to 20;

-C<sub>f</sub>H<sub>2f</sub>C(O)C<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>C(O)OC<sub>g</sub>H<sub>2g</sub>-, -C<sub>f</sub>H<sub>2f</sub>PhC<sub>g</sub>H<sub>2g</sub>-, or -C<sub>f</sub>H<sub>2f</sub>C(O)NHC<sub>g</sub>H<sub>2g</sub>-, wherein f and g are each 1 to 12;

15

and each L is independently a chemical bond or

-C(O)O-, -OC(O)O-, -O-, or -NHC(O)O-, provided that each R is bonded to an oxygen atom of L, and i is an integer from 1 to 3; or X is -C(O)-, each L is a chemical bond, and i is 1.

20

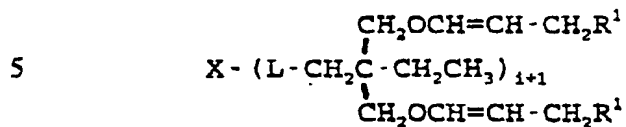
comprising reacting an allyl compound of the formula HO-R-(OCH<sub>2</sub>CH=CHR<sup>1</sup>)<sub>n</sub> with a compound containing a moiety of the formula X-(L-) <sub>i,1</sub> to form an intermediate of the formula X-(L-R-(OCH<sub>2</sub>CH=CHR<sup>1</sup>)<sub>n</sub>) <sub>i,1</sub> and then isomerizing said intermediate to said compound of formula (1) in the presence of an effective amount of a catalyst for said isomerization.

25

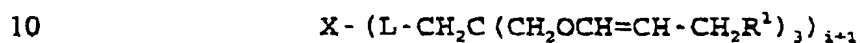
18. A process according to claim 17 wherein R<sup>1</sup> is -H.

30

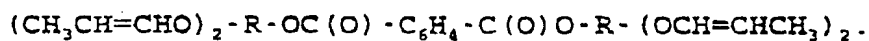
19. A process according to claim 17 wherein said compound has the formula



20. A process according to claim 17 of the formula



21. A process according to claim 17 wherein said compound has the formula



# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 98/17110

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07C43/16 C07C43/215 C07C69/12 C07C69/54 C07C69/96  
C07C271/12 C07C271/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J.V. CRIVELLO & G. LÖHDEN: "The Preparation of Novel 1-Propenyl Ethers and Their Cationic Photopolymerisation" JOURNAL OF POLYMER SCIENCE: PART A; POLYMER CHEMISTRY, vol. 34, no. 10, 1996, pages 2051-2062, XP002086642 see Scheme 2, p. 2056, compounds 1P-9P	3,9,15, 22,27
A	J.V. CRIVELLO: "Design of network polymers by photopolymerisation" DIE ANGEWANDTE MAKROMOLEKULARE CHEMIE, vol. 240, 1996, pages 83-90, XP002086643 see tables 1,2	3,9,15, 22,27

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

### \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*G\* document member of the same patent family

Date of the actual completion of the international search

3 December 1998

Date of mailing of the international search report

09.12.98

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Janus, S

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US 98/17110

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1,2,4-8,10-14,16-21,23-26,28-34  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Claims Nos.: 1,2,4-8,10-14,16-21,23-26,28-34

The general formula (1) is too general and encompasses an extremely broad range of totally different compounds, only partly supported by the examples. For instance, a simple compound such as 2-propenyloxyethanol (RN 33813-91-1 and 33813-92-2) falls within the scope of said general formula. Guided by the spirit of the application as supported by specific disclosure of the examples, the search has been limited to trimethylolpropane dipropenyl ether derivatives.

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**